PHYTOTOXICOLOGY 1996

INVESTIGATION:

UCAR CARBON CANADA INCORPORATED

WELLAND

MAY 1998

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BACKGROUND:

UCAR Carbon Canada Incorporated (UCAR) is a manufacturer of carbon and graphite electrodes used in electric arc furnaces and by aluminum smelters. The facility is located along Canal Bank Road in the southern part of the City of Welland. It consists of several buildings distributed over a 40 hectare (approximately), L-shaped property.

Union Carbide Canada Limited, a related company, produced ferro-alloys at this location since the early part of this century. This part of the business was phased out in the 1970s. More recently, complaints about particulate fallout from the facility have been voiced by residents of the nearby residential community. In the late 1980s the company was convicted of a contravention of Section 14(1) of the Environmental Protection Act. This Section prohibits the release of contaminants that cause or are likely to cause an adverse effect.

The Phytotoxicology Section, at the request of the MOEE Niagara District, conducted investigations in the vicinity of UCAR Carbon Canada Incorporated in 1992, 1993 and 1995. The results of these investigations were reported in:

Phytotoxicology Survey Report: UCAR Carbon Canada Incorporated, Welland (1992 & 1993), Report No. SDB-002-3512-94, July 1994

and

Phytotoxicology Investigation Report: UCAR Carbon Canada Incorporated, Welland (1995), Report No. SDB-020-3511-95, October 1996

The Niagara District office requested another investigation by the Phytotoxicology Section in 1996. These recent requests for investigations were to provide documentation pertaining to effects of atmospheric emissions from UCAR as the company took steps to limit these emissions after being served with a Control Order in February 1994.

MANUFACTURING PROCESS AND EMISSIONS:

Carbon electrodes are produced by mixing calcined anthracite coal or petroleum coke with coal tar pitch. The mix is formed or extruded, and then baked at high temperatures. Graphite electrodes are produced by impregnating the carbon electrodes with more pitch and re-baking.

Due to the nature of the raw materials used and the high temperatures involved, the production of carbon and graphite electrodes can release various organic compounds to the atmosphere.

One such group of compounds are polynuclear aromatic hydrocarbons, commonly known by the acronym, PAH. Chemically, these compounds consist of carbon and hydrogen atoms in two or more fused benzene rings. The properties of individual PAH compounds are determined by the number and orientation of these rings. The Appendix to this report contains representations of the molecular structures and some physical properties of 16 common PAHs.

PAHs are formed during incomplete combustion of organic materials, or whenever organic materials are exposed to high temperatures. In nature, PAHs are formed in forest and grass fires, and during volcanic activity. Anthropogenic sources include fossil fuel combustion and industrial processes, such as coke production. As a consequence, PAHs are commonly encountered in surface soil of large urban centres, especially those with PAH emitting industries.

PAHs are considered semi-volatile compounds. The boiling points of the compounds listed in the Appendix range from 218° C for the double-ring naphthalene, to in excess of 500° C for the six-ring PAHs. In the atmosphere, PAHs are absorbed onto suspended particulates. Only the lightest PAHs with relatively low boiling points have a significant vapour phase.

In the environment, PAHs will undergo photo-degradation and metabolism by micro-organisms. The rates at which these reactions occur depend on the reaction conditions as well as the relative complexity of the PAH molecule. Consequently, PAH concentrations in environmental media will diminish over time, once the source is removed.

INVESTIGATION DESIGN:

The investigation was conducted on September 11, 1996. It consisted of a collection of foliage from silver maple trees located throughout the primarily residential neighbourhood bounded by Ontario Road, Southworth Street, Humberstone Road, and Dain Avenue. This investigation was virtually a repetition of the one conducted in 1995.

The design of the 1996 investigation evolved from those conducted previously. In 1992 and 1993, silver maple foliage samples were collected beyond the bounds of the neighbourhood described above. Those investigations revealed that the effects of UCAR emissions were not detectable beyond that neighbourhood. The 1995 investigation focused all of the sampling in this neighbourhood to define the area measurably impacted by PAH emissions from UCAR and to establish a baseline from which compliance with the Control Order could be monitored. For the 1996 investigation, one new sampling location was added and sampling at one existing location was modified to provide a sample with a more direct exposure to emissions from UCAR.

Figure 1 shows the locations of the 21 sampling locations, numbered 16 through 36, used during the 1996 investigation. Previous investigations included locations 1 through 15. Also shown are the UCAR buildings.

Silver maple was used in this investigation because it was the most common deciduous tree species in the neighbourhood. Airborne particulates containing the condensed PAH compounds, will be deposited onto the foliage over the course of the growing season. While these particulates are subject to removal by wind and rain action, there is a predominant tendency for accumulation of contaminants in tree foliage near a point source over the course of the growing season. Uptake of PAHs from the soil would be negligible since they are not readily absorbed through roots or translocated within plants.

SAMPLING AND ANALYTICAL PROCEDURES:

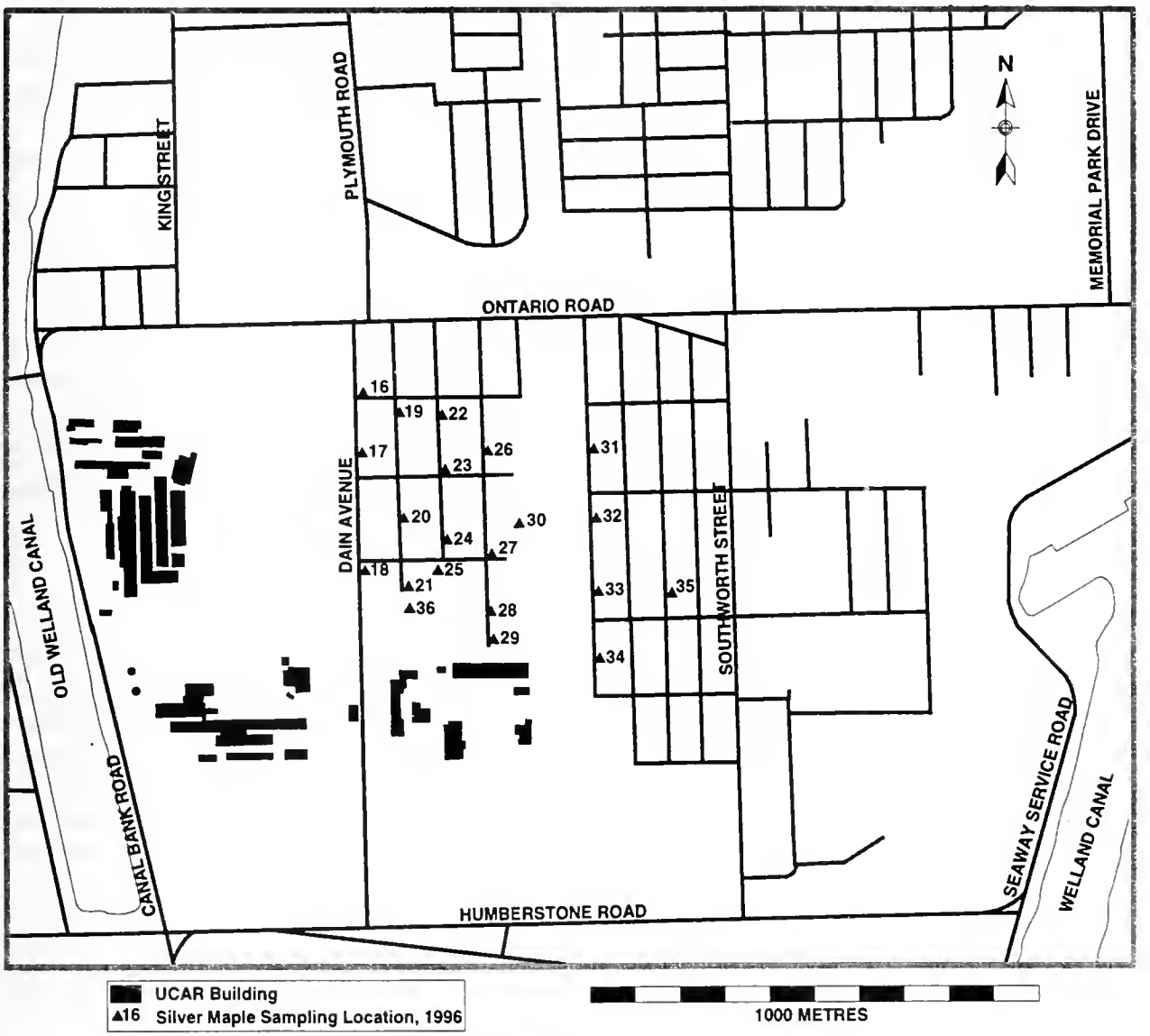
A tree foliage sample was obtained by using a branch pruner mounted on an extendable pole to cut a branch from the sample tree canopy. The branch was cut from the side of the canopy that faced UCAR at a height of between five and ten metres from the ground. Approximately 20 leaves were removed and cut into fragments, approximately five square centimetres in size, using stainless steel scissors. The leaf fragments were mixed in a stainless steel bowl and transferred to a labelled amber glass jar.

Prior to sampling, all equipment that would contact a sample was washed with a laboratory detergent solution, rinsed with distilled water, and then sequentially rinsed with

acetone and hexane. The glass jars, which would contain the samples, had aluminum foil lining on the lid and had been solvent-washed by the analytical laboratory.

The foliage samples were delivered to the MOEE Laboratory Services Branch (LSB) with a request to determine the concentrations of the PAH compounds listed in the Appendix.

Figure 1: Location of 1996 Sampling Sites - UCAR Carbon Canada Incorporated Survey



RESULTS:

. The concentrations of the individual PAH compounds in each foliage sample, in units of nanograms per gram (ng/g) of fresh weight, are listed in the table on the following page. Seventy-six percent of the foliar concentrations of PAHs were below the analytical detection limits, indicated by the code '<W'. Another 22% were qualified with the code '<T', indicating a measurable trace quantity. The remaining two percent were not qualified.

The 'Net Total' PAH concentrations reported in the table were calculated by summing the sixteen individual PAH concentrations in each sample as reported by LSB, without regard for the qualifiers, and subtracting 400 ng/g. The 400 ng/g value is the sum of the sixteen '<W' detection limits. This procedure was used in the previous reports and summarizes the sixteen data points for each sample in a single datum. Figure 2 compares the 'Net Total' concentrations in samples collected during the 1995 survey with those from the same trees collected during the 1996 survey.

Currently, there are no guidelines for PAHs in urban street tree foliage, nor is there an understanding of what PAH concentrations may be phytotoxic. Based on limited sampling by the Phytotoxicology Section, the detection of PAHs in tree foliage above the '<W' level indicates the presence of a PAH source.

PAH Concentrations (nanograms per gram, fresh weight) in Silver Maple Foliage

UCAR Investigation, September 11, 1996, Welland

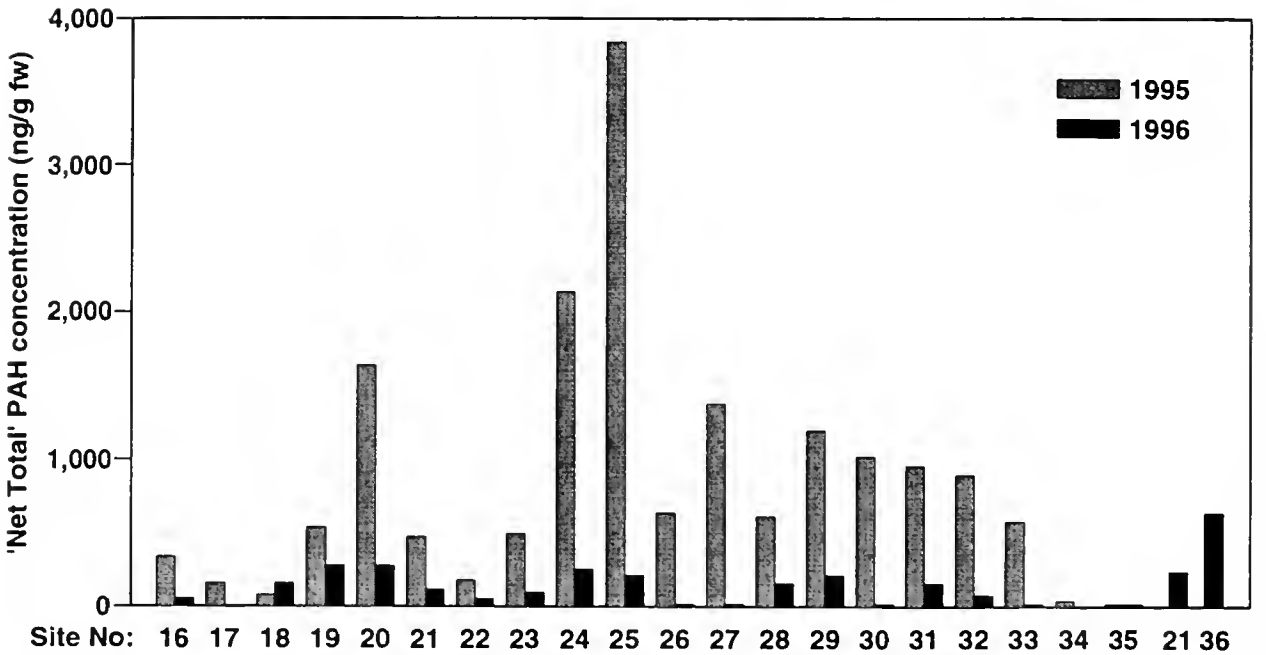
PAH	Site 16	Site 17	Site 18	Site 19	Site 20	Site 21	Site 21	Site 22	Site 23	Site 24	Site 25
Naphthalene	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Acenaphthylene	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Acenaphthene	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Fluorene	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Phenanthrene	20 <W	20 <W	40 <T	20 <W	40 <T	20 <W	20 <W	20 <W	20 <W	20 <W	40 <T
Anthracene	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Fluoranthene	40 <T	20 <W	60 <T	100	80 <T	20 <W	60 <T	40 <T	40 <T	40 <T	60 <T
Pyrene	40 <T	20 <W	40 <T	100	80 <T	20 <W	60 <T	40 <T	40 <T	40 <T	60 <T
Benzo(a)anthracene	20 <W	20 <W	40 <T	60 <T	40 <T	40 <T	40 <T	20 <W	40 <T	40 <T	40 <T
Chrysene	40 <T	20 <W	60 <T	80 <T	80 <T	60 <T	100	40 <T	60 <T	80 <T	60 <T
Benzo(b)fluoranthene	20 <W	20 <W	40 <T	40 <T	60 <T	60 <T	60 <T	20 <W	40 <T	60 <T	80 <T
Benzo(k)fluoranthene	20 <W	20 <W	20 <W	20 <W	40 <T	40 <T	40 <T	20 <W	20 <W	40 <T	20 <W
Benzo(a)pyrene	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	20 <W	80 <T	40 <W
Benzo(g,h,i)perylene	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	80 <T	40 <W
Dibenz(a,h)anthracene	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W
Indeno(1,2,3-cd)pyrene	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W
NET TOTAL	**60**	**0**	**160**	**280**	**280**	**120**	**240**	**60**	**100**	**260**	**220**

The two columns for Site 21 contain data for samples collected from a sheltered and an exposed part of the canopy, respectively.

PAH	Site 26	Site 27	Site 28	Site 29	Site 30	Site 31	Site 32	Site 33	Site 34	Site 35	Site 36
Naphthalene	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Acenaphthylene	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Acenaphthene	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Fluorene	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Phenanthrene	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	40 <T
Anthracene	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W
Fluoranthene	20 <W	20 <W	60 <T	80 <T	20 <W	60 <T	40 <T	20 <W	20 <W	20 <W	100
Pyrene	20 <W	20 <W	60 <T	60 <T	20 <W	60 <T	40 <T	20 <W	20 <W	20 <W	100
Benzo(a)anthracene	20 <W	20 <W	40 <T	40 <T	20 <W	40 <T	20 <W	20 <W	20 <W	20 <W	60 <T
Chrysene	40 <T	40 <T	80 <T	100	40 <T	60 <T	60 <T	40 <T	20 <W	40 <T	160
Benzo(b)fluoranthene	20 <W	20 <W	20 <W	40 <T	20 <W	40 <T	20 <W	20 <W	20 <W	20 <W	140
Benzo(k)fluoranthene	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	20 <W	60 <T
Benzo(a)pyrene	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	80 <T
Benzo(g,h,i)perylene	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	80 <T
Dibenz(a,h)anthracene	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W
Indeno(1,2,3-cd)pyrene	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	40 <W	80 <T
NET TOTAL	**20**	**20**	**160**	**220**	**20**	**160**	**80**	**20**	**0**	**20**	**640**

<W no measurable response
<T a measureable trace amount

Figure 2: 'Net Total' PAH Concentrations in Silver Maple Foliage, 1995 vs. 1996



DISCUSSION:

As was mentioned in a preceding section, the 1995 and 1996 investigations around UCAR were intended to provide a mechanism by which PAH emissions from this source could be monitored as the company complied with the Control Order. Previous investigations had delineated the extent of measurable effects. The 1995 investigation had established a baseline of foliar PAH concentrations against which future investigation results could be compared. The 1996 investigation was intended to reaffirm this baseline as well as clear up some discrepancies in the PAH foliar concentration pattern. Note that the company had not yet instituted any new emission controls during the period of these investigations.

The results of the 1996 investigation revealed substantially lower foliar PAH concentrations than were encountered in 1995. Such an observation frequently suggests a substantial reduction in emissions by the subject source. However, a review of the ambient air PAH data shows that air concentrations preceding the 1996 investigation were very similar to those preceding the 1995 investigation. The air monitoring station is located near Site 28.

When contaminant concentrations approach analytical detection or quantification limits, it becomes imprudent to correlate the concentration data which other variables, such as proximity to the suspect source. For that reason, contaminant contour mapping was not conducted with the 1996 data, as was done with the 1995 data. Two observations are worth highlighting, however.

The foliar PAHs at Site 36 are about two or three times as high as at the next highest sites. Site 36 was established during the 1996 investigation and is the nearest site to the UCAR production buildings in the southern arm of their property. This site is in the 'park' that, according to posted signs, is UCAR property, but is open to the public for recreational use.

The second observation pertains to two samples collected at Site 21. In 1995, PAHs at this site were uncharacteristically low when compared to other sites nearby. It was thought that

the sampled part of the canopy might have been sheltered by other trees. Therefore, in 1996, samples were collected from the same part of the canopy as well as another part that was directly exposed to the UCAR buildings. The 'exposed' sample from Site 21 had higher PAH concentrations than the 'sheltered' sample.

These observations, while continuing to point to UCAR as the source of PAHs deposited onto tree foliage, do not contribute to resolving the great discrepancy between the data from 1995 and 1996. To see if climatic variables may have influenced the observations, precipitation records for Welland were obtained from the Atmospheric Environment Service of Environment Canada. On September 7 and 8, 1996, the Welland meteorological observation station recorded a total of 93 millimetres of rain. This is an exceptionally heavy rainfall in such a short time period. This rainfall preceded the September 11 sampling by three days.

In 1995 the sampling took place on September 7. Prior to that sampling, the only significant rain storm (as opposed to rain shower) was a 43.4 millimetre event 27 days previously.

It appears that the major rainfall preceding the 1996 sampling by three days was instrumental in washing the particle-bound PAHs off the foliar surfaces.

CONCLUSIONS AND RECOMMENDATIONS:

This investigation was unable to fulfill its primary objective of reaffirming the baseline concentrations of PAHs in tree foliage around the UCAR operation. It appears that an extraordinary rainfall preceding the sampling day was responsible for very effectively washing the particles containing absorbed PAHs from the leaf surfaces. This is a reasonable explanation for the substantially lower foliar PAH concentrations in 1996.

This investigation warrants repeating in 1997, but it is critical that meteorological events be considered when planning the sampling date. A September date is still desirable because it is near the end of the growing season. If 1997 investigation confirms that PAHs are present on tree foliage in the vicinity of UCAR, then subsequent investigations can be used to indirectly monitor compliance with the Control Order.